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Preparation of hydrophobic $CaCO_3$ composite particles by mineralization with sodium trisilanolate in a methanol solution†

Dong-Ki Keum, Kyung-Min Kim, Kensuke Naka* and Yoshiki Chujo*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University,
Yoshida, Sakyo-ku, Kyoto, 606-8501, Japan. E-mail: ken@chujo.synchem.kyoto-u.ac.jp

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Hydrophobic $CaCO_3$ composite particles were prepared *via* crystallization of $CaCO_3$with a sodium trisilanolate [$(c\text{-}C_5H_9)_7Si_7O_9(ONa)_3$] in methanol. The molar ratio of calcium ion to the sodium trisilanolate was varied from 0.1 to 0.5. FT-IR and TGA analysis of the obtained product indicated that the trisilanol was bound to the crystalline $CaCO_3$. By changing the concentration of the trisilanol, composite particles with different shapes and polymorphism were obtained. Low concentration of the trisilanol gave stable vaterite crystals, the polymorph of which did not change when the composite was kept in water for more than 1 week. The contact angle of the modified vaterite was $62 \pm 4°$. Dispersability of the composites in a polystyrene matrix was significantly improved compared with a bare $CaCO_3$. We have succeeded in surface modification of particles with the hydrophobic trisilanolate.

Introduction

Recently, the synthesis of organic–inorganic hybrids by mimicking biomineralization has attracted great attention.[1] The proteins that have been found to be associated with biominerals are usually highly acidic macromolecules. It has been known that organic additives introduced to the crystallization process of $CaCO_3$ modify the shapes of crystals.[2,3] On the basis of specific interactions, small molecules or synthetic anionic polymers have been found to be potent inhibitors or habit modifiers of crystal morphology by absorption onto the surface of the growing crystal and inhibition of the growth of a particular crystal face, thus controlling their growth rate and habit through the strength and selectivity of this adsorption.[4–10] The control of the crystal shape and structure of calcium carbonate is also important to its industrial uses as pigments, pastes, and abrasives and in paper and plastic as a filler. Surface modification of calcium carbonate with hydrophobic species would lead to a great expansion in these applications, since mineral particles are hardly dispersed in a polymer matrix.[11]

The last few decades have seen further developments in the chemistry of incompletely condensed polyhedral oligosilsesquioxanes, and the use of the oligosilsesquioxanes containing more than one hydroxyl group is becoming important as building blocks for many metallasiloxanes.[12–15] Of particular interest have been reactions of trisilanols with ligand-deficient trivalent metal complexes because the inability of these trisilanols to support trigonal planar coordination environments is expected to produce more complex structures.[16–19] We expected that the trisilanols might have strong interaction with inorganic surfaces, and have the potential to control the nucleation and growth of inorganic crystallites. The strong coordination ability of the oligosilsesquioxanes may enable the design and synthesis of composites in which $CaCO_3$ surfaces are coordinated to a group of the trisilanols. Although many studies have shown that a wide range of additives can influence the shape of crystals under laboratory conditions, the trisilanols have not been used for the crystallization of $CaCO_3$. In the present work, we studied the crystallization of $CaCO_3$ in the presence of a sodium trisilanolate [$(c\text{-}C_5H_9)_7Si_7O_9(ONa)_3$] and found that hydrophobic $CaCO_3$ composite particles were obtained.

Experimental section

Materials

A trisilanol [$(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$] (**1**) was prepared by the method of Feher *et al.* reported previously.[20] Calcium chloride, ammonium carbonate, polystyrene ($M_w = 10000$), and sodium hydroxide were purchased from WAKO Pure Chemical Industries, Ltd.

Crystallization of $CaCO_3$

Sodium hydroxide (the feed ratio of sodium hydroxide to **1** was 3 : 1) was added to 90 ml of a methanol solution of the trisilanol. After addition of the sodium trisilanolate solution to the methanol solution was completed, 2.47 ml of each aqueous reactant solution (0.1 M $CaCl_2$ and 0.1 M $(NH_4)_2CO_3$) were added *via* syringe into the solution of the sodium trisilanlolate at 30 °C under N_2. This solution was kept at 30 °C under N_2 for one day with gentle stirring. This solution was transferred into a centrifugal tube and the following sequence was repeated three times; centrifuging, decanting the supernatant, addition of fresh methanol, and mixing by shaking. Finally, the supernatant methanol was decanted and the remaining product was isolated after drying in a vacuum oven at 50 °C for one day. Hydrophobic $CaCO_3$ composites were purified as follows. The product was suspended in tetrahydrofuran (THF) by vigorous stirring for 3 min. The dispersed product in THF was isolated from the sedimented part by decantation and dried in a vacuum oven at 50 °C for one day.

Preparation of $CaCO_3$/polystyrene composite

The $CaCO_3$/polystyrene composites were prepared by spin coating on the glass from a mixture of $CaCO_3$ (10 wt%) with polystyrene (0.2 g) in toluene (2 ml) and drying at 100 °C for 24 h.

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†Electronic supplementary information (ESI) available: Fig. S1–S3. SEM micrographs of the $CaCO_3$–polystyrene composites. See http://www.rsc.org/suppdata/jm/b2/b204490k

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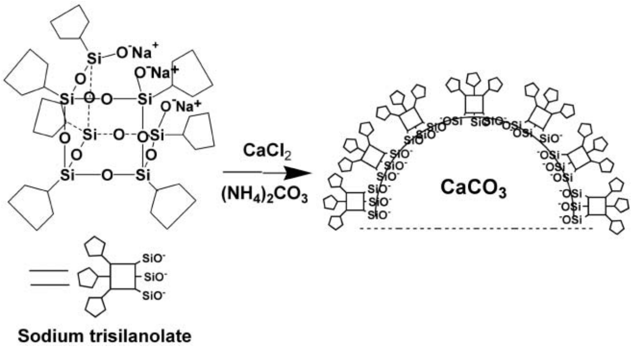

Fig. 1 Preparation of hydrophobic $CaCO_3$ composites by mineralization with sodium trisilanolate in a methanol solution.

Measurements

Scanning electron microscope (SEM) measurement was carried out using a JEOL JSM5310/LV at 15 KV. X-Ray diffraction measurements were made on a Shimadzu XRD-6000 in $\theta/2\theta$ mode at room temperature. The 2θ scan data were collected at 0.02° intervals and the scan speed was 2° (2θ) $\min^{-1}$. FT-IR was recorded by using a Perkin Elmer system 2000 employing a KBr pellet method. TGA was performed on a Shimadzu DT-30 Instrument with a heating rate of 10 °C $\min^{-1}$ under an air atmosphere. The contact angle against water on a horizontal surface of a pellet was measured at 25 °C with a Kyowa Kaimen Kagaku CAD type goniometer. A powdery sample (1 g) was pressed into pellet form.

Results and discussion

Mineralization of $CaCO_3$ with the sodium trisilanolate in a methanol solution was studied (Fig. 1). 2.47 ml of each reactant (0.1 M $CaCl_2$ and 0.1 M $(NH_4)_2CO_3$) were injected *via* syringe into 90 ml of the methanol solution of the sodium trislanolate at 30 °C. A sudden increase in the turbidity of the homogeneous solution was observed during addition of the calcium reactants. The concentration of the calcium reactants was constant in all experiments. The molar ratio of calcium ion to the trisilanol was varied from 0.1 to 0.5. After the crystalline product was suspended in THF by vigorous stirring, a dispersed phase and a sedimented part were separated by decantation. The sedimented product was shown to be mainly $CaCO_3$ by TGA analysis. The THF dispersion was filtered and dried to give a purified product. The experimental conditions and the results are summarized in Table 1.

Fig. 2 shows FT-IR spectra of the obtained products.[21,22] All samples show a Si–O–Si asymmetric stretching vibration at 1088 cm^{-1} and a strong absorption occurring around 1414 cm^{-1} which is characteristic of calcium carbonate. These results indicate that the trisilanol was bound to all the crystalline $CaCO_3$. T01 shows a strong band at 746 cm^{-1} as well as a carbonate out-of-plane bending vibration at 876 cm^{-1}, which indicates vaterite formation. The IR spectrum of aragonite shows a carbonate out-of-plane bending vibration at 856 cm^{-1}, the band of which is observed in the IR charts of T025 and T05.

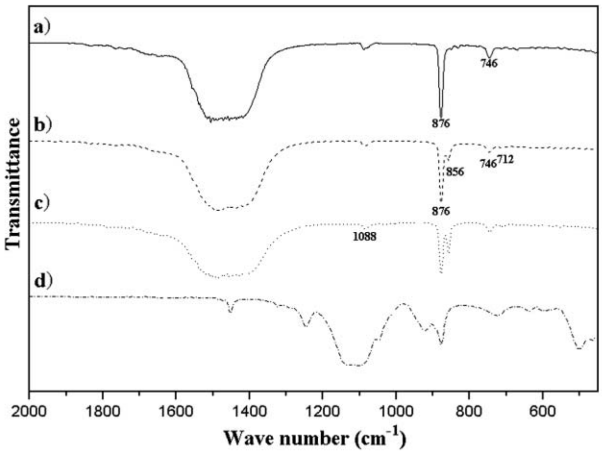

Fig. 2 IR spectra of (a) T01, (b) T025, (c) T05, and (d) trisilanol.

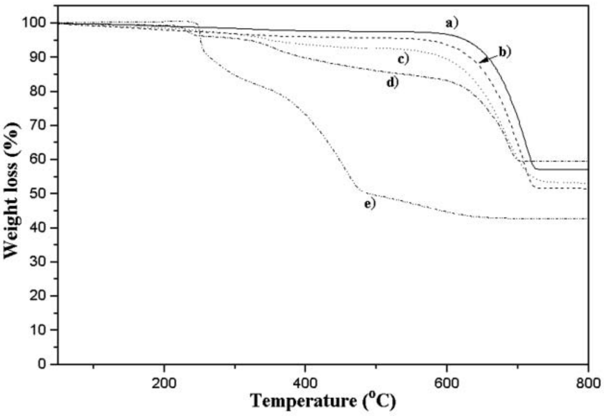

Fig. 3 TGA of (a) T0, (b) T01, (c) T025 (d) T05 and (e) trisilanol.

The TGA analysis for the crystalline $CaCO_3$ obtained in the presence of the trisilanol gave a larger weight loss at 250–600 °C compared with that of the pure $CaCO_3$ (Fig. 3), which was due to the decomposition of the organic moieties of the trisilanol. These results are also shown in Table 1. It was reported that weight loss at 600 °C of pure aragonite particles is about 3 wt%,[21] similar to that of T0. The trisilanol contents of T01, T025, and T05, which were roughly estimated according to the weight loss at 600 °C, were 9, 16, and 32 wt%, respectively. The trisilanol content increased with increasing feed ratios of the trisilanol to the calcium reactants.

The crystal phases of the particles were examined by X-ray diffraction (XRD) (Fig. 4).[23] The XRD pattern of T05 shows strong and weak reflections corresponding to aragonite and vaterite, respectively. The intensity of the reflection corresponding to vaterite decreased from T01 to T05 (Fig. 4(a)–(c)). In the case of T01, the polymorphs of $CaCO_3$ were entirely vaterite (Fig. 4(a)).

Table 1 Characterization of T0–T05, produced by changing the concentration of the trisilanol

Run	Sample	Molar ratio of $CaCO_3$: trisilanol	Yield (%)[a]	Weight loss at 600 °C (%)[b]	Contact angle[c]/°	Polymorphism
1	T0	1 : 0	68[d]	3	25±2	Vaterite
2	T01	1 : 0.1	23[e]	7	62±4	Vaterite
3	T025	1 : 0.25	19[e]	10	68±3	Vaterite > Aragonite
4	T05	1 : 0.5	20[e]	17	75±5	Aragonite > Vaterite

[a] Estimated on the basis that all the trisilanol and the calcium carbonate were recovered. [b] Calculated by TGA (Fig. 2). [c] Average of three independent experiments. (±standard deviation). [d] Isolated yield without THF treatment. [e] Isolated yield after THF treatment as described in the Experimental section.

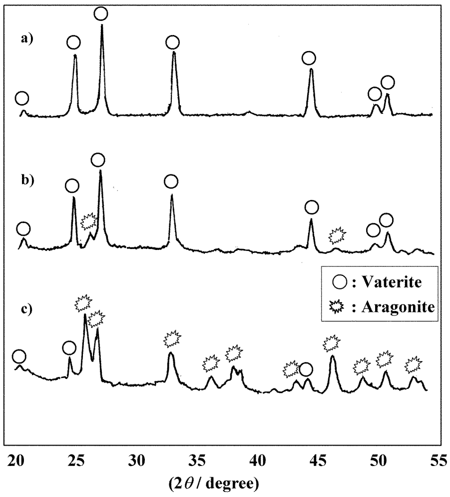

Fig. 4 XRD patterns of (a) T01, (b) T025, and (c) T05.

The morphologies of the crystals are shown in the SEM micrographs (Fig. 5(a)–(d)).[24] Vaterite particles of T01 were rice-form crystals. The average particle diameter was 1–2 μm. The rice-form vaterite particles were also observed in T025 and T05. Irregular-shape crystals as an aggregate of several nanocrystals coexisted in T025 and T05. The irregular-shape crystals in T025, T05 should be aragonite. The active surface sites for the crystal growth might be inhibited by the trisilanol.

Although the crystal polymorph of T0 was transformed to calcite when T0 was kept in an aqueous solution at room temperature for 2 days, the crystal polymorph did not change when T01 was kept in an aqueous solution at room temperature for more than 1 week. It is well known that vaterite transforms easily and irreversibly into thermodynamically more stable forms when in contact with water.[25] The complete phase transformation of vaterite usually occurs within 80 h. We speculated that the vaterite surface was protected by the trisilanol, preventing phase transformation in an aqueous solution. On the basis of these observations, we expected that the surface of the particles was modified with hydrophobic cyclopentyl groups. The influence of organic additives on the nucleation and critical growth of $CaCO_3$ has been studied by a number of authors. Several organic molecules with carboxylate, phosphorus, or sulfate anions inhibit phase transitions of metastable phases.[3,9,26] Strong coordination sites of three silanolate anions in the trisilanolate might strongly bind to vaterite crystals.

The precipitation of $CaCO_3$ in the absence of the trisilanol was carried out in methanol under the same conditions described above. The crystalline $CaCO_3$ (T0) obtained was vaterite. SEM observation of T0 shows similar shape as that of T01. It was already reported that the presence of ethanol, isopropanol, and diethylene glycol affects the rates of spontaneously precipitated vaterite and stabilizes this polymorph preventing the transformation to the thermodynamically stable calcite.[27] Therefore, vaterite formation is favorable in non-aqueous solvents.

In the case of T01, such low concentrations of the trisilanol had no influence on the nucleation and growth of vaterite. However, the amount of the trisilanol may be sufficient to block all active surface sites of the vaterite particles. It is speculated that many attached trisilanolates around vaterite crystals play a role as the protector, preventing phase transformation to calcite in an aqueous solution. In the presence of the trisilanol, a sudden increase in the turbidity of the homogeneous solution was observed after addition of the calcium reactants was completed. In the presence of the trisilanol, precipitation of $CaCO_3$ was observed during addition of the calcium reactants. Higher concentration of the trisilanol showed a marked acceleration of the crystallization. At higher concentration, the trisilanol captured calcium ions and increased local concentration of the calcium reactant to promote the nucleation of $CaCO_3$. Aragonite might be kinetically induced by the higher amount of the trisilanol in methanol.

The interaction characteristics of the modified $CaCO_3$ surface were measured by contact angle (Table 1). The experiments consisted of contacting a 1 g pellet of compacted composites with water. Contact angle measurements provide a good qualitative approach, which indicates that the trisilanol

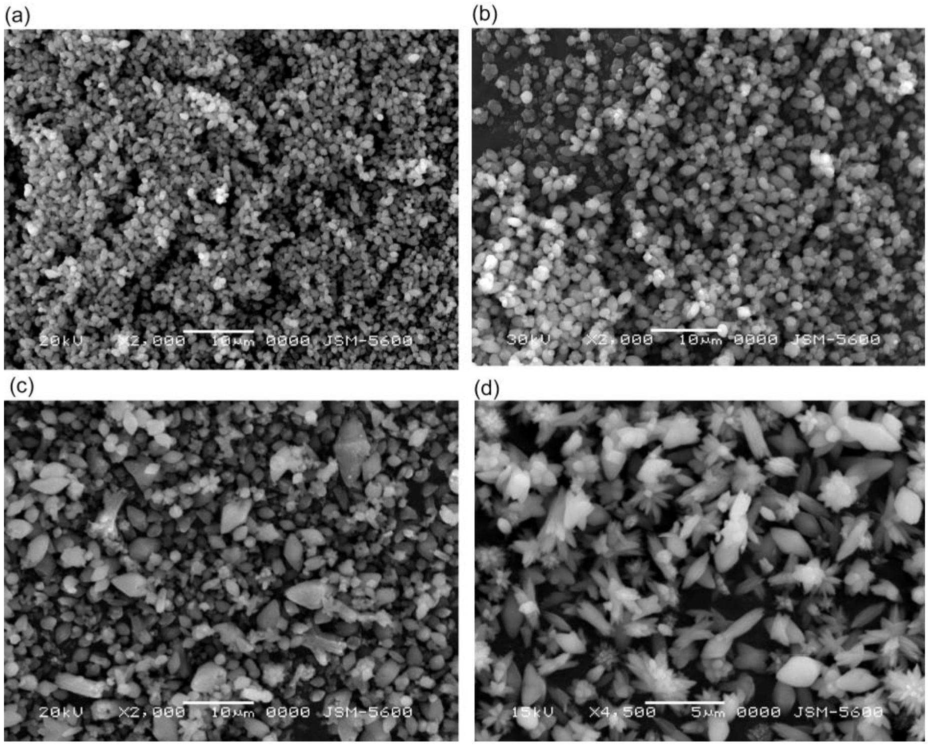

Fig. 5 SEM micrography of (a) T0, (b) T01 (c) T025, and (d) T05.

Table 2 Dispersibility of T1 and T01 in organic solvents

		Sedimentation time/min[a]	
Run	Solvent	T0	T01
1	THF	5	90
2	Toluene	1	35
3	Cyclohexane	< 1	120
4	Hexane	< 1	50

[a] Sedimentation time was determined using a dispersed solution (10 wt%) at room temperature.

changed the $CaCO_3$ surface character. Higher surface coverage of the trisilanol with $CaCO_3$ yielded higher contact angles suggesting an increased hydrophobic surface of the $CaCO_3$ composite. The contact angles of the pellets after drying at 100 °C for 24 h were not changed, which indicates that no volatile compounds were present in the samples.

The characteristics of trisilanol covered $CaCO_3$ are also shown in Table 2. The dispersabilities of T01 in organic solvents were significantly improved compared with that prepared without the trisilanol .

After drying the samples, composites containing 10 wt% each of T0, T01, and T025 were prepared by mixing with polystyrene in toluene. The surfaces of the $CaCO_3$/polystyrene composites were analyzed by SEM (Fig. S1–S3, see ESI†). Aggregation of the $CaCO_3$ particles was observed in the case of T0 (Fig. S1). When T01 and T025 were used, however, each particle of $CaCO_3$ was well dispersed in the polystyrene film (Fig. S2 and S3). These results suggested that the hydrophobic particles improve dispersibility in the polymer matrix.

Conclusion

We have succeeded in surface modification of $CaCO_3$ particles with the hydrophobic trisilanolate. By changing the feed ratio of the trisilanol to the calcium reactants in methanol, hydrophobic inorganic–inorganic composites with different shapes and polymorphism were obtained. The trisilanolate has an interesting nanosized cage structure derived from the direct one step hydrolytic condensation of cyclopentyltrichlorosilane.[20] It contains three anionic ligands which can be strongly attached to the $CaCO_3$ crystals and also shows enhanced hydrophobicity caused by the seven cyclopentyl groups on the trisilanol. Low concentrations of the trisilanol gave stable vaterite crystals covered with the hydrophobic species. Vaterite is the thermodynamically most unstable of the three crystal systems, calcium, aragonite and vaterite, and occurs scarcely in nature. Vaterite is expected to useful for various purposes, since it has features such as high surface area, high dispersion, and low specific gravity compared with the other two crystal structures. The present stable monodispersed spherical vaterite particles would be expected to be excellent as stable pillaring precursors in several polymer matrixes.

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